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13. ABSTRACT *(Maximum 200 Words)*

This project involves a novel approach to the synthesis of new classes of materials designed to function as ion conducting systems. In particular, our aim is to synthesize materials for use as polymer electrolytes in solid-state lithium batteries. The current phase of this proposed work is designed to identify promising candidates and to study the mechanism by which ions are transported through these new solids. The ultimate goal is to produce a working lithium battery incorporating the new electrolytes.

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Program Title: Supramolecular Engineering of New Lithium Ion Conducting Polymer Electrolytes.

Principal Investigator: John Arnold, University of California, Berkeley.

Agreement Number: F49620-01-0498

Objectives
The aim of this project is to investigate a novel approach to the synthesis of new classes of materials designed to function as ion conducting systems. In particular, our aim is to synthesize materials for use as polymer electrolytes in solid-state lithium batteries. The current phase of this proposed work is designed to identify promising candidates and to study the mechanism by which ions are transported through these new solids. The ultimate goal is to produce a working lithium battery incorporating the new electrolytes.

Nanomembranes
Nanoporous methacrylate polymer membranes were prepared from solution grown zinc oxide nanowire array templates. Poly(methyl methacrylate-co-glycidyl methacrylate) and Poly(t-butyl methacrylate-co-glycidyl methacrylate) were made by radical polymerization and deposited on the zinc oxide array by spin coating. A photo acid generator was used to crosslink the film. The template was dissolved in mild acidic conditions and the resulting films were characterized by SEM. Initial lithium ion conductivity measurements were obtained by AC impedance.

Previous work has been carried out using bulk polymerizations of methyl methacrylate (MMA) on the substrate, vapor deposition of parylene-C, and spin coating of uncrosslinked poly-(methyl methacrylate) PMMA. It has been our goal during the last year to develop a system which demonstrates the optimal filling found in the spin coating procedure while also yielding a robust crosslinked film. In order to realize this route, new polymers had to be developed that incorporated functionality that could be crosslinked by an initiator included in the polymer solution. The easiest way to achieve this was with a UV sensitive moiety. To fill this role, a photo acid generator (PAG), $SPh_3^+SbF_6^-$, incorporated into the polymer mixture. The two polymers conceived to exploit this initiator are shown in Scheme 1.
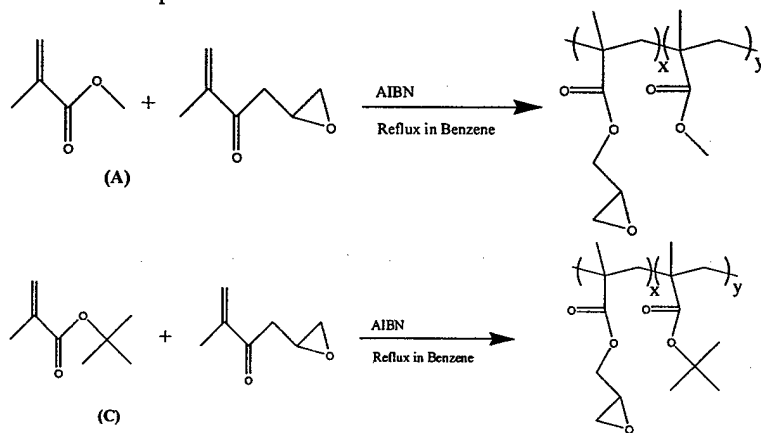
Scheme 1. Polymerization schemes for methacrylate copolymers with photo crosslinkable functionalities.

The glycidyl methacrylate was chosen as the crosslinking moiety which can undergo acid catalyzed ring opening polymerization reactions. The methylmethacrylate was replaced with the acid labile t-butyl methacrylate to give access to the free acid for later functionalization.

Having synthesized the methyl methacrylate/ glycidyl methacrylate copolymers, the spin coating procedure was optimized for the following parameters: percent polymer in solution, percent PAG in solution, spin rate, and spin time. For 3 μm thick arrays, the optimal spin coating procedure was to use 25% polymer in solution at a spin rate of 700 rpm for 40 seconds, this provides just less then complete filling which is ideal for creating the polymer films. The amount of PAG used in the solution has no effect on the filling characteristics, rather it influences the degree of crosslinking found in the final film. This variable was examined after testing the solubility of the films, and it was found that 10% PAG by weight of the polymer gives stable cross linked films.

After heating to evaporate any excess anisole and exposing to UV light (253 nm) to initiate the crosslinking reaction, a free standing film can be obtained upon dissolution of the nanowire array in 1 M HCl. The resulting film has been characterized by scanning electron microscopy (SEM).
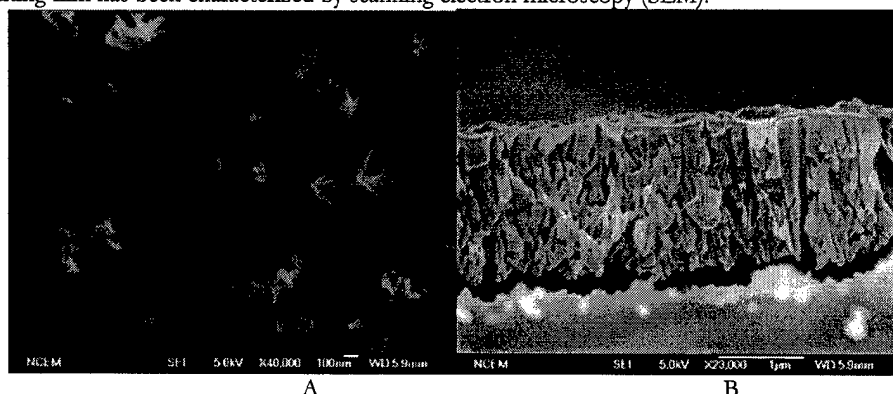

<div align="center">A   B</div>

Figure 1: **A.** Top view of a crosslinked poly(t-butyl methacrylate-co-glycidyl methacrylate) porous polymer film after the ZnO nanowire array has been dissolved in HCl. **B.** A cross-section of the same polymer film. The polymer films have been coated in 10 Å of gold to prevent charging in the SEM.

The crosslinking of this film has been tested by exposing it to a number of organic solvents and observing dissolution and swelling behavior. A film which has not been crosslinked will be soluble in anisole and many other organic solvents. When 10% PAG is used in the initial formulation, there is no change to the polymer after 24 hours in anisole or propylene carbonate, but limited dissolution in acetone, and pronounced swelling in THF.

The lithium ion conductivity of these porous polymer films has been tested using AC impedance in collaboration with the Kerr group. Since the methacrylate polymer films will not be lithium conductors on their own until functionalized, the pores were filled with lithium salts dissolved in propylene carbonate. These initial results are a reference for our material before further organic modification is pursued within the pores. The bulk conductivity of our films was roughly 4×10^{-5} S/cm. By calculating the density of pores within our membrane (1.1×10^9 pores/cm) an effective conductivity within the pores can be estimated. The effective pore conductivity of our sample was found to be 1.8×10^{-3} S/cm. This is slightly lower than the value reported for bulk propylene carbonate $4\text{-}6 \times 10^{-3}$ S/cm. This can be rationalized by taking into account the interactions of the propylene carbonate with the pore walls, which will increase the viscosity of the propylene carbonate within the pore compared to the bulk.

Current work is focusing on the functionalization of these pores according to the scheme below. Work in the Fréchet group on the synthesis of chiral HPLC supports has helped to develop a synthetic scheme for the modification of the t-butyl methacrylate/ glycidyl methacrylate polymer films[1-3]. The t-butyl group of the t-butyl methacrylate monomers can be cleaved in acidic conditions, followed by a DCC coupling with the appropriate polyether, which should yield functionalized nanochannels. Then to insure the stability of these channels to lithium, any residual, unreacted carboxylic acid groups will be reacted with iodomethane.
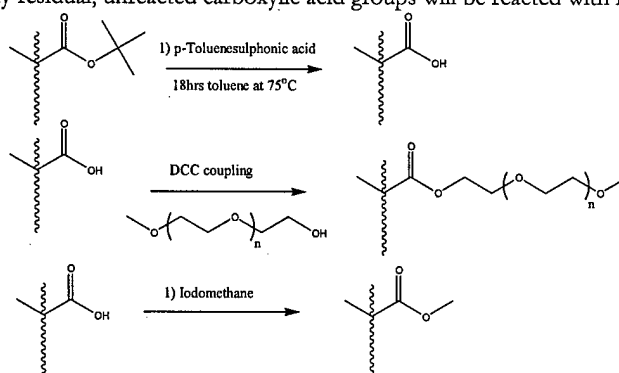
Scheme 2: Proposed modification procedure for the porous polymer membrane derived from the t-butyl methacrylate/ glycidyl methacrylate copolymer. The methylation step will be necessary to cap any of the free acid moieties.

A further method to create inorganic films with ordered pore structures is anodization of aluminum. Anodically oxidized aluminum has been examined for use in filtration and evaporation masks in addition to as a template for nanowire growth. Porous alumina has desirable mechanical properties – it is hard and uniformly thick and has moderate brittleness and flexibility. Alumina is also electrically insulating and is able to maintain its mechanical and dielectric properties over a wide temperature range. The technique of anodization furnishes the alumina films with a uniform array of pores arranged in hexagonal cells. A high pore density is achieved (up to 10^{15} per m^2) and the pores have consistent diameter. In addition, there is great flexibility in pore diameter (4-250 nm) and film thickness (0.1-300μm) depending on fabrication conditions.

Porous alumina is an attractive material for the intended purpose due to reproducibility in creating continuous channels of a uniform size through the material. Samples of porous alumina have been prepared by the anodization of aluminum according to a previously described method. Polished aluminum samples were anodized at 30 V in oxalic acid for 39-44 hours, which afforded porous alumina membranes with 40 nm diameter pores that were continuous and approximately 60 μm deep (excess aluminum is removed chemically as well as the barrier layer) (See Figure 2).

The conductivity of an alumina membrane was tested after it had been soaked in a liquid electrolyte, 1 M solution of Li TFSI in propylene carbonate/ethylene carbonate (PC/EC) (1:1), for 5 days. If the membranes are not able to conduct ions through their pores with a liquid electrolyte present, it seems unlikely that they will be able to conduct ions when functionalized and no liquid is present. The conductivity results are presented in Table 1.
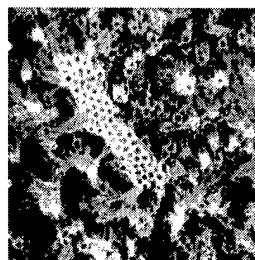

Figure 2. SEM image of porous alumina membrane with 40 nm diameter pores.

The room temperature conductivity is on the order of 10^{-5} S/cm. These results show that transport through the channels is possible, but that conductivity is currently below useful levels. The membrane tested had a thickness of approximately 60 μm. To improve conductance, the membranes can be made much thinner, which is accomplished with shorter anodization times. Future work on the alumina membranes will entail functionalization of the pores and treatment of the membrane with a lithium salt before making impedance measurements.

Temperature (°C)	Conductivity (S/cm)
30	1.35 x 10^{-5}
42	2.11 x 10^{-5}
50	5.43 x 10^{-5}
60	4.81 x 10^{-5}
70	6.92 x 10^{-5}

Table 1. Conductivity data for porous alumna membrane (40 nm diameter pores, 60 μm thick, 1 cm^2 area.)

Yang has shown that it is possible to fabricate polymer membranes with silica nanotubes embedded in them. They have grown silicon nanowires via chemical vapor deposition, oxidized the wires to give an SiO$_2$ sheath, deposited parylene, and then performed several etching steps until left with silica nanotubes in a parylene membrane. This method ensures that there are continuous channels through the membrane. The silica nanotubes can be functionalized and a lithium salt introduced to form a solid electrolyte material. Using a similar idea, the Arnold and Yang groups wish to create porous nanomembranes of a variety of materials, including polymers and silica derived from sol gel reaction, for use in developing lithium ion battery electrolyte materials.

Preliminary conductivity measurements have been made on the silica nanotube/parylene membranes. The samples were prepared on doped silicon substrates (resistivity 0.01-0.4 Ohms·cm) so that the membranes would not need to be removed from the substrate for use in conductivity measurements. Samples were placed in a dry box for several days to removed adsorbed water. One sample, used as prepared, was placed in a stainless steel cell and its impedance measured. The sample exhibited no measurable conductivity. Two samples were soaked in a 1M solution of LiTFSI in propylene carbonate/ethylene carbonate (1:1) for 3-5 days in the dry box. Samples were placed in stainless steel cells. In this system, one electrode is the stainless steel cell and the other is the doped silicon. Impedance measurements were taken at various temperatures. The results are presented in Table 2.

Temperature (°C)	Conductivity Membrane 1 (S/cm)	Conductivity Membrane 2 (S/cm)
30	1.92×10^{-6}	5.70×10^{-8}
40	1.47×10^{-6}	7.02×10^{-8}
50	1.25×10^{-6}	8.31×10^{-8}
60	1.25×10^{-6}	9.37×10^{-8}
70	1.18×10^{-6}	1.18×10^{-8}
80	2.35×10^{-6}	1.18×10^{-8}
90	2.42×10^{-6}	1.47×10^{-8}
100	2.35×10^{-6}	1.66×10^{-8}

Table 2. Conductivity of silica nanotubes/parylene membrane. (7 μm thick, area 1 cm².)

Even though it is promising that these materials do conduct, the conductivites are much too low to be considered useful. Two alterations would improve the conductance: decreasing the thickness of the films (right now they are 5-7 μm) and increasing the pore density of the membrane. By increasing pore density, the area of material through which ions can flow is increased. Future work on these systems will involve functionalization of the inner walls of the silica tubes and introduction of a lithium salt to make an all solid electrolyte system. Even if the conductivity is low it may be possible to make a membrane thin enough such that the conductance is high enough for use in battery systems.

Porous nanomembranes are also being fabricated by depositing sol gel onto a nanowire array. This process eliminates the need to include a template molecule in the sol gel synthesis and ensures that the pores are continuous through the membrane. The most promising candidate for the nanowires is ZnO because of the relative ease in creating large arrays of well aligned nanowires. One drawback is that ZnO dissolves in both acidic and basic conditions making it necessary to bring the sol gel near neutral pH before depositing onto the wires.

A process identical to the synthesis of a CTAB templated sol gel with ethanol as co-solvent was employed. The only alteration was that CTAB was not added. The final sol gel solution had pH ~6 so the pH of the sample was not adjusted. The sample was spin coated onto a ZnO nanowire array on silicon substrate. The sample was also diluted (5 parts ethanol and 1 part sol gel solution) and the diluted sample was spin coated onto a nanowire array. One drop of the diluted sample was also put onto a nanowire array using a pipette, with the assumption that capillary action would pull the sol gel into the spaces between the wires.

After the samples had dried, they were analyzed by field emission scanning electron microscopy (FESEM). Looking at the surface of the samples, there is no major difference in appearance vs. ZnO nanowire arrays with no sol gel. Some regions of the sample with the diluted drop appear to have thick coverage. Therefore, samples were broken and cross-sections were examined by FESEM. Cross-section analysis showed that there was not good coverage of the sol gel material by spin coating processes. The samples that were spin coated with diluted and undiluted sol gel material both showed poor coverage, blank areas, and regions where globs of the material sits on top of the wires (Figures 3-4).
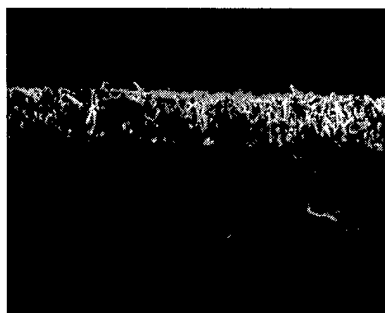
Figure 3. SEM of diluted sol gel material spin coated onto a ZnO nanowire array, 11,000x magnification.
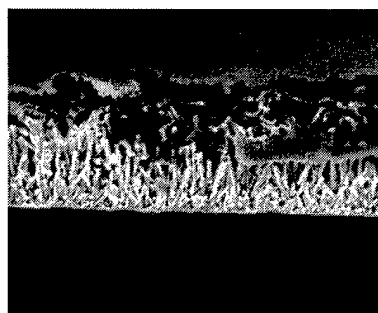
Figure 4. SEM of sol gel material spin coated onto a ZnO nannowire array, 25,000x magnification.

The sample that received one drop of diluted sol gel material by pipette also did not have complete coverage. However, larger portions of the sample were covered than either of the spin coated samples. The wires were covered with the sol gel from top to bottom showing that capillary action pulled the sol gel material into the spaces between wires. However, there were still vacant areas so this capillary action was not a perfect process. In addition, there are areas where the wires are completely covered but no longer appear well aligned (Figure 5).
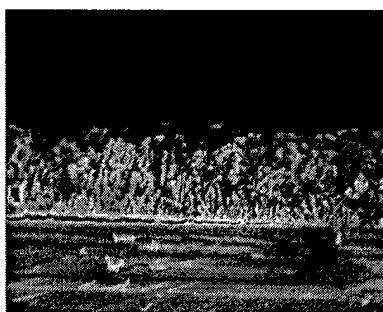

Figure 5. Scanning electron micrograph of dilute sol gel material as dropped onto a ZnO nanowire array, 19,000x magnification

This sample also had interesting features. Where the wires are completely covered in silica, the silica and nanowire membrane begins to lift off of the silicon substrate surface. The lift off indicates that there may be possibilities for freestanding films created in this manner (Figures 6-7).
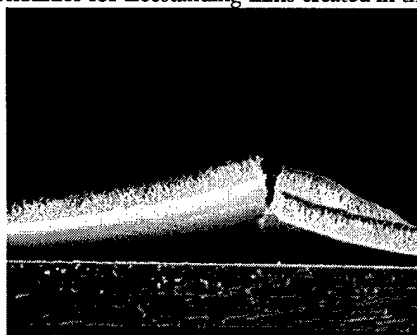
Figures 6-7.SEMs of dilute sol gel material as dropped onto ZnO nanowire array, 4,000x and 3,700x magnification respectively. These micrographs show the lift off feature of the material.

One possibility for this lift off is that the diluted sol gel material partially dissolves the wires, which allows them to pull from the substrate. A more likely reason is that as the sol gel dries, solvent evaporates and incurs dimensional changes in the material. Perhaps these dimensional changes are sufficient to pull the nanowires from the substrate.

Once the process of fabricating these nanowire/silica membranes is improved to increase the sol gel coverage, the next step would be to dissolve the ZnO nanowires from the membrane. If no part of the nanowires is exposed, it will be necessary to etch the silica to expose the ZnO. The ZnO can then be dissolved using acidic or basic media, leaving behind a silica nanomembrane with channels running through it. Once this step is complete, the silica can be functionalized and treated with a lithium salt and conductivity measurements taken.

Surfactant-templated Mesoporous Channel Materials.
Two types of templated sol gel reactions have been explored this year. The first is an aqueous sol gel method requiring no co-solvent, using published procedures as guides. TMOS was used as the silica source, cetyl trimethyl ammonium bromide (CTAB) as the templating agent, and HCl as the hydrolysis catalyst. Though TMOS is not soluble in water, the use of CTAB eliminates the need for a co-solvent. A typical synthesis, which results in an ordered system, has a TMOS: water mole ratio of 1:8 and a TMOS: CTAB mole ratio of 1:0.08 (or greater). Films were cast by spin coating onto glass microscope slide covers to give clear, smooth, and continuous films. There was slight cracking at the edges of the films, but this may be due to the process of spin coating onto a square substrate. Figure 8 shows an XRD spectrum of a film with TMOS: CTAB ratio of 1:0.12. XRD confirms that this method produces ordered systems.
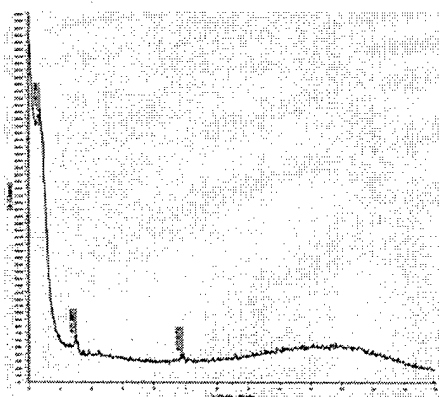

Figure 8. XRD spectrum of silica film prepared according to the CTAB templated sol gel with no co-solvent method. TMOS:CTAB ratio is 1:0.12 and TMOS:water ratio is 1:8.

TEM samples were prepared by sonication in isopropyl alcohol. It was not possible to visualize well-defined pores with TEM, indicating that the system is no longer ordered and that preparation of the samples for TEM somehow affected or collapsed the pores. Portions of the sample do show electron diffraction patterns, but the values calculated for d-spacing are too small to be the spacing between mesopores. Energy dispersive spectroscopy (EDS) was used to determine the composition of the samples producing diffraction. The portions that show diffraction patterns contain no silica, just metal contamination. Portions of the sample were also found to produce electron diffraction ring patterns. EDS shows that these samples do indeed contain silicon and oxygen, but that aluminum is also present. The XRD results, on the other hand, reveal reasonable values for d-spacing (the largest spacing being at least 30 Å) which are in the range of literature reported values.(P,N)

Columnar Liquid Crystals.
The liquid crystal approach was taken because the required species may be synthesized by conventional small molecule techniques but yield ordered macroscopic materials. A variety of liquid crystal phases are known, and we expect aligned columnar phases and cubic phases to be the most useful for our applications. We are focusing on producing aligned columnar phases. Of our several approaches to lithium ion electrolytes, we expect these materials to be the most similar in physical dimensions to natural ion channels as each pore opening should be several angstroms across (just larger than the metal ion), and the entire pore forming molecule several tens of angstroms across. The two main challenges of this design are designing a material that forms the desired phases as well as creating a pore opening that is not too strongly binding to the metal ion.

It has already been shown that some liquid crystalline materials have higher lithium ion conductivities in the mesophase than in the isotropic phase,[4] and that alignment of the liquid crystalline domains can further raise conductivities.[5] These past examples have mostly suffered from low conductivities as well as inadequate

stabilities to radicals, heat and reducing conditions. We are attempting to address the problem of low conductivities by making materials that bind less strongly to lithium ions than the literature examples. Most of the instability in the literature compounds occurs in materials with benzyl functionality and so we are avoiding this and other similarly unstable structural components.

We began with cyclic salen-like molecules of type **1**. This structure was chosen as a large number of metal salen liquid crystal complexes are known and it was our hope that a lithium complex would form analogous materials. Although we found that the core structure **1a** is able to bind lithium ions, which was confirmed in the solid state by X-ray crystallography and indicated in solution by nuclear magnetic resonance and cyclic voltammetry, none of the derivatives of this material that we have investigated have formed mesophases.

1a R = H
**1b** R = OC$_8$H$_{18}$
1c R = N(C$_8$H$_{18}$)$_2$
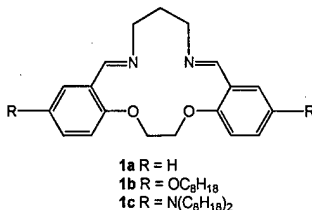
Greater success has been had with a member of the family of compounds **2**. The aza-14-crown-4 derivative **2a** was not observed to produce any mesophases either alone or in the presence of lithium salts. The aza-15-crown-5 derivative, however, shows more interesting phase behavior over a range of lithium hexafluorophosphate concentrations. Interestingly the compound shows only simple solid to isotropic phase transitions neat or as the lithium triflate complex. This is in contrast to literature examples where the identity of the anion has only minimal effect on the phase behavior unless the anion is large (as in the case of TFSI). In the case of the LiPF$_6$ complexes in the 0.2-0.5 equivalents salt range we observe several phase transitions on both the heating and cooling cycles using differential scanning calorimetry (DSC). Optical microscopy of these materials reveals that they are birefringent, and thus ordered, over the entire range investigated (room temperature to 120° C, above this upper limit the salt complexes decompose). Besides birefringence we also observe fluid-like flow under the microscope indicating a mesophase, but have not been able to identify the phase yet. We are currently seeking additional means, such as variable temperature X-ray powder diffraction to assist us in identifying the phase.

2a n = 1
2b n = 2
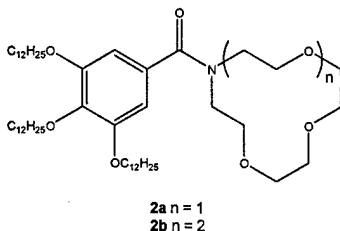
While working on phase identification, we have also begun conductivity studies on two salt complexes of **2b**. We have made the 2:1 and 4:1 ligand to salt complexes on a larger scale and cast them from solution onto 1 cm^2 stainless steel electrodes between a 123 micron spacer and measured their conductivity by AC impedance over a range of temperatures. Results are presented in Table 1. Each value is an average of data from two identically prepared cells. We find much higher conductivity for the 4:1 complex, with room temperature conductivity estimated in the range of 10^{-3} S·cm^{-1}, while the 2:1 complex appears to have room temperature conductivity on the order of 10^{-4} S·cm^{-1}. While these conductivities are high, several factors should be taken into account. First, these are molecular materials and the liquid crystal phase, while more viscus than carbonate electrolytes, still exhibits fluid behavior. High conductivity is expected from liquid electrolytes and once we have made a thin film from a cross-linkable analog we expect a lower conductivity. On the other hand no attempt has been made to align the samples and if conductance in these materials involves passing ions from crown to crown then aligning the material should increase conductivity in both the molecular and cross-linked materials.

| Temperature, °C	Conductivity S·cm⁻¹	
	4:1 Ligand to LiPF$_6$	2:1 Ligand to LiPF$_6$
35	2.51E-03	5.34E-04
45	5.25E-03	1.41E-03
55	1.05E-02	4.41E-03
65	1.80E-02	5.66E-03
75	3.05E-02	8.54E-03

We have recently also produced a new crown-ether containing material **3**, which is closely related to a series of mesogenic compounds reported by Goodby and coworkers.[6] The uncomplexed material has several low temperature phase transitions, which we are currently identifying. We are also preparing a variety of lithium salt complexes to test their phase behavior.
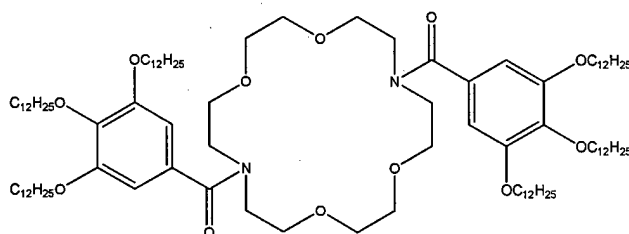
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As we had reported previously we have produced a number of molecules of increasing complexity which contain crown-ethers in the hopes of creating liquid crystalline materials which self assemble into channel-like structures. While we were able to realize our synthetic goals, we have to date only created low ordered materials which do not exhibit the phase behavior we had intended. Over the course of the work we did, however, identify a crown-moiety which is solution exhibits a high lithium exchange rate (we were not able to completely decoalese the lithiated and free ligand signals even at -80° C and do not have an exact rate of exchange). Our original proposal included producing crown-ether containing polymers for lithium-ion conduction so we have applied the knowledge gained from the liquid crystal work to this area.

We have produced the monomer, **5**, for our first polymer in this series and are ready to make the polymer. With the polymer in hand we will be able to make salt complexes and conductivity measurements regardless of weather the material exhibits any liquid crystalline behavior (which it was not specifically designed to).
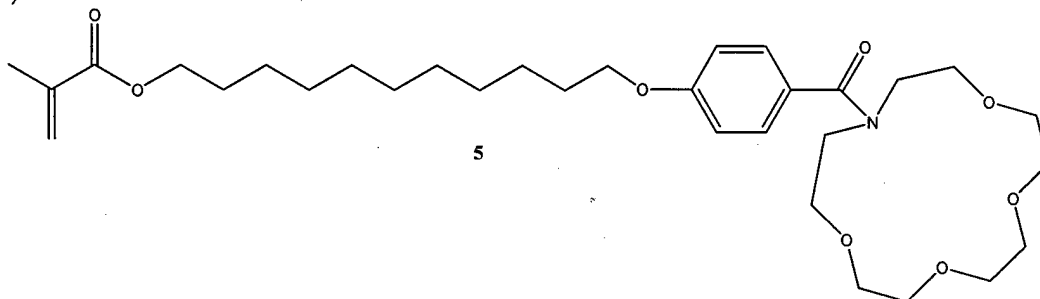
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Although work in the Kerr group has already shown that acrylate type polymers are not stable to lithium electrodes in DC cell cycling measurements,[7] we can still make measurements with AC impedance. By changing the alkyl chain length between the polymerizable end of the molecule and the crown-ether head group we hope to be able to measure conductivities of a range of materials above and below their glass transition temperatures in order to gain insight into the mechanism of ion transport in such systems.

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